THE DIELECTRIC PROPERTIES OF WATER

AT 35,000 MEGACYCLES

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THE DIELECTRIC PROPERTIES OF WATER AT 35,000 MEGACYCLES

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On the completion of this work I wish to express my appreciation to my wife for the many times she aided me as my laboratory assistant in the experimental measurements. In addition, I should like to thank Dr. J. E. Boyd, Head of the Physical Sciences Division of the Engineering Experiment Station, without whose cooperation and assistance I could not have pursued this research.

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SUMMARY

The index of refraction (n) and the absorption coefficient (k) of water were determined by experimental measurements at a frequency of 35,000 Mc. From these experimental values the complex dielectric constant, $K' - jK''$ of water was determined from the expression $K' - jK'' = (n - jk)^2$. The power source was a reflex klystron modulated by a 2.5 kc. square wave. The attenuation between two horns submerged in water was measured, as the horn separation was varied, by the use of a calibrated attenuator and a crystal detector whose output was amplified in a high gain amplifier. Observations were made at intervals of 5 degrees over a temperature range of 0° - 50°C.

The object of the measurements was to provide experimental verification of the theoretical Onsager modified equations relating to the electrical properties of dipolar liquids. The data obtained fill a gap in existing observations.

INTRODUCTION

Considerable information has been published about the dielectric properties of water at frequencies below 24,000 Mc. A thorough knowledge of its electrical properties at higher frequencies seems desirable. In the present investigation the properties of water were studied at a frequency of 35,000 Mc. and over a temperature range of zero to fifty degrees centigrade. The results are compared with Onsager's theoretical equation and Saxton and Lane's[1] experimental values.

The dielectric properties of water at microwave frequencies have been the subject of numerous investigations. Many of the early observers used radiation sources which produced damped waves. The results so obtained are not considered reliable because of the uncertainties of frequency measurement and spectral energy distributions. The advent of radar has considerably advanced the techniques of microwave equipment and measurements; as a result, it is now possible to obtain excellent quantitative data.

Debye[2] as early as 1929 was able to account theoretically for the dielectric properties of polar gases and dilute solutions in non-polar solvents by the application of the internal field theory of Clausius and Mosotti. This theoretical treatment, when applied to polar liquids such as water, gave results contrary to those determined experimentally. As a consequence, modifications of this earlier work have been presented by Frohlich[3], Onsager[4], Kirkwood[5], and many others. In general, the modified theory has attempted to present a more complete theoretical model by adding the effects of dipolar interaction and

the polarization due to atomic vibrations which were neglected in the original theory. Since the relaxation time of the molecule must be measured experimentally, any quantitative results derived from theory are really only semi-theoretical in nature.

The microwave dielectric properties of water are generally expressed in terms of a complex dielectric constant, as follows:

$$K = K' - jK''$$

$$K = K' - 2j\sigma/f$$

$$K = (n - jk)^2$$

where σ is the conductivity, f is the radiation frequency, n is the index of refraction, and k is the absorption coefficient. Thus, the dielectric properties may be described in terms of the conductivity or the optical constants n and k.

In the present tests the attenuation and phase shift of free-wave radiation through the dielectric medium are measured. The values in the above equations are then derived from the observed quantities.

THE RELATIONSHIP BETWEEN THE OPTICAL CONSTANTS AND THE DIELECTRIC CONSTANTS

The general wave equation for the electric field, E, in an uncharged and unbounded lossless dielectric medium is

$$\nabla^2 E = \mu \varepsilon \frac{\partial^2 E}{\partial t^2} \tag{1}$$

where μ* and ε are respectively the permeability and the permittivity of the medium. A particular solution of (1) is

$$E = E_o e^{j\omega(t - (\mu\varepsilon)^{1/2} z)} . \tag{2}$$

This solution represents a wave traveling in the z direction the velocity, v, of which is given by

$$v = 1/\sqrt{\mu\varepsilon} . \tag{3}$$

Equation (2) may be written in terms of the velocity of an electromagnetic wave in free space, c, and the index of refraction of the medium, n, as

$$E = E_o e^{j\omega(t - nz/c)} . \tag{4}$$

In a dielectric medium such as water, which has attenuation, the index of refraction may be replaced by a factor termed the complex index of refraction, n - jk, where k is the absorption coefficient. With this

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*In the subsequent development it is assumed that the permeability, μ, of the medium is equal to μ_o, the permeability of free space.

substitution equation (4) becomes

$$E = E_o e^{j\omega[t - (n - jk)z/c]}. \tag{5}$$

From this it is seen that the wave traveling in the z direction may be represented by the exponential expression

$$E = E_o e^{-\omega kz/c} \cdot e^{j\omega(t - nz/c)}. \tag{6}$$

This expression is equivalent to

$$E = E_o e^{-\alpha z} \cdot e^{j(\omega t - \beta z)} \tag{6a}$$

where the attenuation constant is

$$\alpha = \omega k/c \text{ nepers per meter} \tag{7}$$

and the phase constant is

$$\beta = n\omega/c \text{ radians per meter.} \tag{8}$$

Converting these expressions to more conventional engineering units*, one sees that the rate at which the amplitude of the wave decreases in the z direction is

$$\alpha = \frac{2\pi \times 8.686\ k}{\lambda_o} \text{ decibels per millimeter} \tag{9}$$

from which

$$k = 0.01835\,\lambda_o \alpha. \tag{9a}$$

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*1 neper = 8.686 decibels.

Similarly, in a dielectric medium of index of refraction, n, the phase constant β is determined by the relation

$$\beta = 2\pi n/\lambda_o \qquad (10)$$

therefore

$$n = \lambda_o \beta/2\pi \quad \text{radians per millimeter} \qquad (10a)$$

From equations (9a) and (10a) one is able to calculate the index of refraction and the absorption coefficient of a liquid as accurately as the attenuation and phase shift can be measured. Furthermore, no absolute readings are required since a given reference position and a known change of path length, Δz, will give the quantities required for calculation.

It is usual to regard the dielectric constant as equal to the square of the optical index of refraction. This amounts to saying that the total polarization of the molecule is due to only the electronic polarization. As will be seen in the following section of the theory of dielectrics, this is not strictly true of polar molecules such as water. Therefore, if the complex dielectric constant, K, is defined as the square of the complex index of refraction, then

$$K = K' - jK'' = (n - jk)^2 . \qquad (11)$$

By separately equating the real and imaginary components one may obtain

$$K' = n^2 - k^2 \qquad (12)$$

and

$$K'' = 2nk. \tag{13}$$

Equations (9a) and (10a) are the expressions which lead to the development of an experimental system for the measurement of the dielectric properties of water. With values measured and tabulated from these expressions, together with equations (12) and (13), it is possible to calculate the complex dielectric constant of a dielectric medium having loss at very high radio frequencies.

EXPERIMENTAL METHOD AND PROCEDURE

The experimental measurements were made at a frequency of 35,000 Mc. (8.57 mm wavelength) produced by a QK 191 reflex klystron oscillator. The klystron was amplitude modulated by a 2.5 kc. crystal-controlled square wave, fed from an electronically stabilized power source, and cooled by an air blower. The variation of r-f signal was detected by a 1N26 crystal whose output was indicated on a vacuum tube voltmeter. Figure 1 shows a block diagram of the essential parts of the experimental system. Figures 2 and 3 are photographs of the experimental system used for these measurements.

Since the attenuation of water at 35,000 Mc. is of the order of 180 db per centimeter, any experimental system involving transmission through the medium must use very short path lengths. Figure 4 shows the water cell and the two electromagnetic horns between which the measurements were made. The faces of the horns were made water tight by a thin slab of polystyrene and placed face to face in the water cell as shown. The receiving horn on the right was positioned by means of a micrometer so that its variation in position was known with great accuracy. The change in parallelism of the two horns over the movements involved was not measurable.

The temperature of the water was maintained at specified values within the cell by use of a circulating pump and manual control of the flow through coils of copper tubing immersed in a temperature bath. The effects of phase and amplitude variation were recorded over a temperature range of 0°-50° Centigrade for known increments of path length in the dielectric medium.

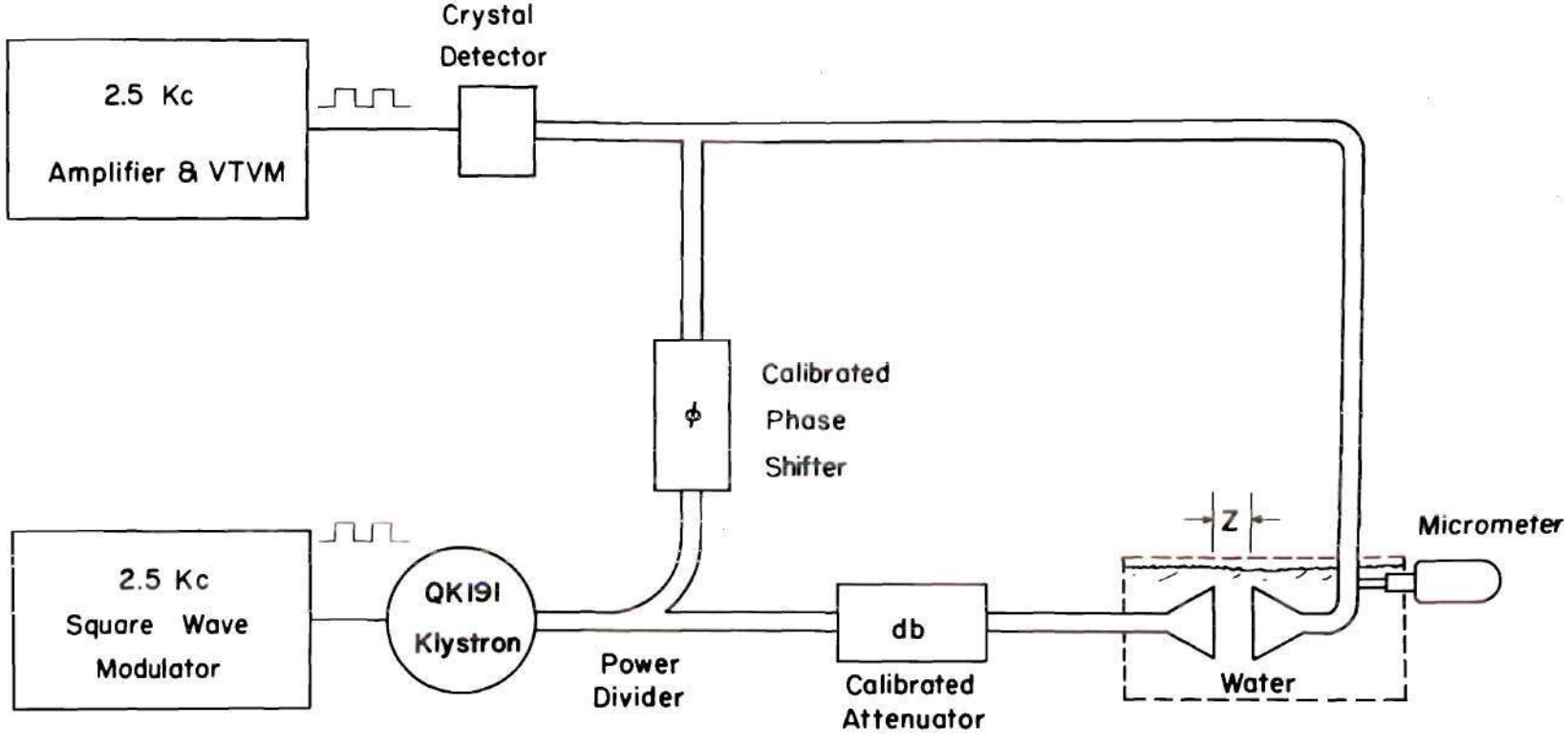


Figure 1

Experimental System

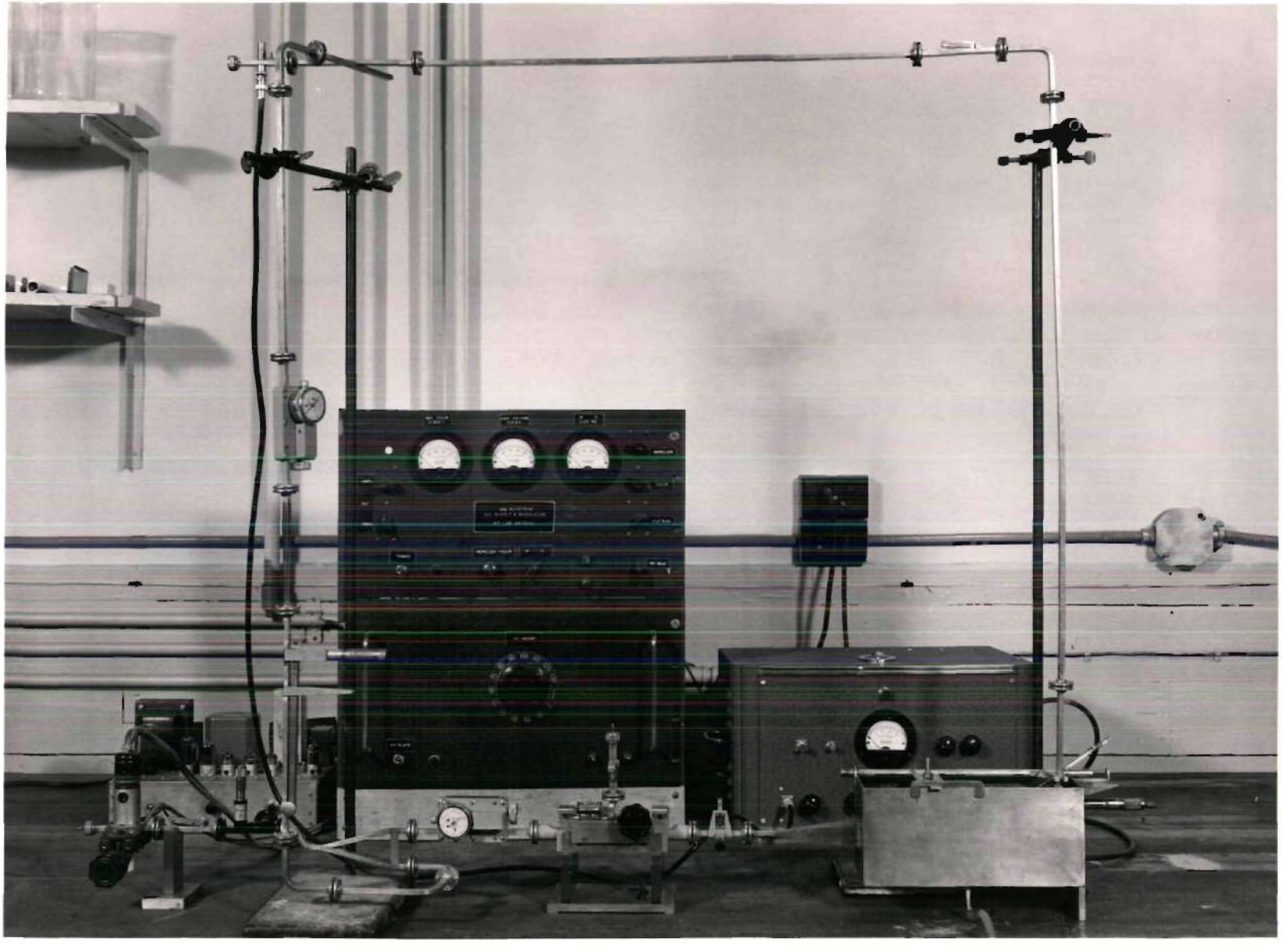


Figure 2

Laboratory Equipment for the Measurement of
Attenuation and Phase Shift of Water

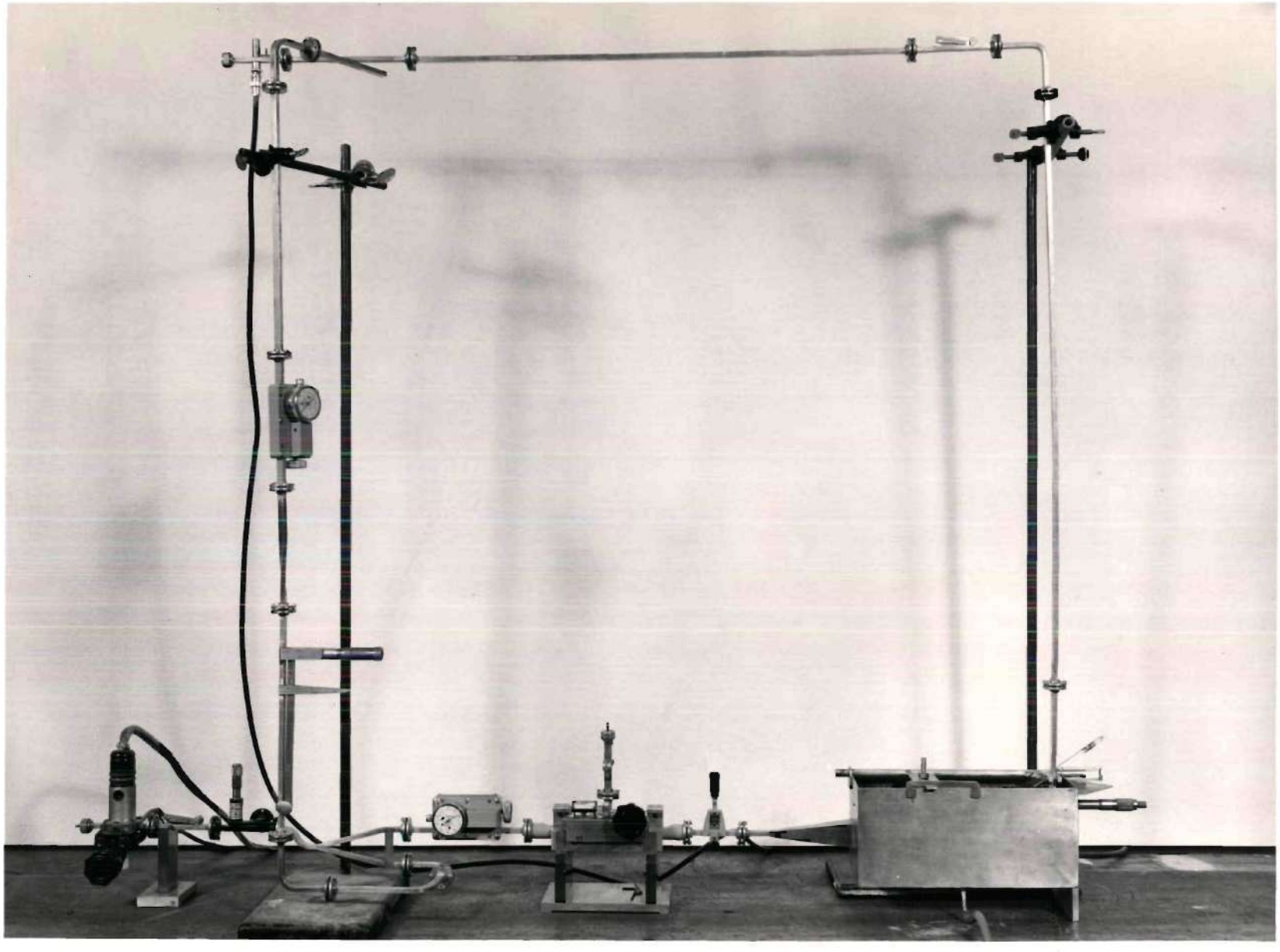


Figure 3

Laboratory Equipment for the Measurement of
Attenuation and Phase Shift of Water

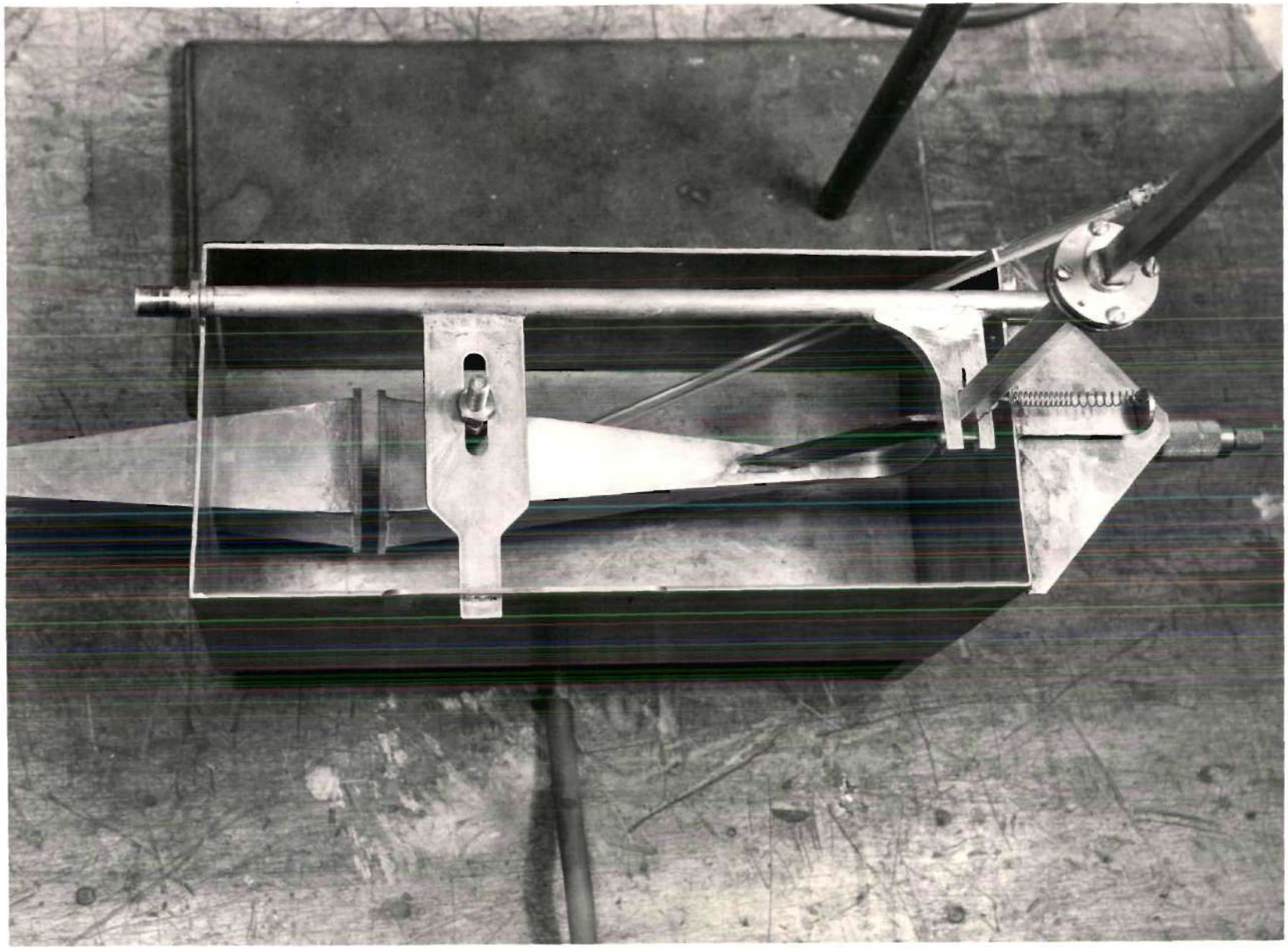


Figure 4

The Water Cell and Electromagnetic Horns

The frequency was maintained constant at 35,000 ± 5 Mc. by manual control with reference to a tunable calibrated cavity connected directly to the transmission line. The limit of accuracy was imposed by the bandwidth of the cavity.

The experimental measurements involved finding two quantities; the absorption in db per millimeter, and the phase shift in radians per millimeter, as the two horns were positioned at various known separations. The method requires no knowledge of absolute transmitted power but only a reference power or reference phase as given by the initial separation of the horns.

For measurement of absorption, the waveguide containing the phase shifter was essentially removed from the circuit by placing 60 db of attenuation in the line containing it.

The reference reading for each temperature was determined by removing all the attenuation in the main line leading to the horns and separating them to the maximum spacing that still gave a reliable signal at the crystal detector. This separation was of the order of 3 mm for all temperatures. As the path length was decreased in steps of 0.2 mm, by moving the horns closer together with the micrometer, the signal was held constant at the crystal detector by inserting attenuation with the calibrated attenuator. The small increments of distance were used merely for check purposes, so that a large number of readings were averaged for the final result at each temperature. This procedure also provided a constant check on the equipment, necessary since absorption must vary linearly in db with distance for the measurements to be valid. This method has the advantage of a constant signal at the crystal and thus

obviates the necessity for crystal calibration, a tedious and often inaccurate process.

The phase measurements were made at similar increments of distance. The signal was divided between the calibrated phase shifter and the water cell and then recombined in a directional coupler which fed the crystal detector. In the interest of obtaining maximum sensitivity, the signals through the water and the phase shifter were made equal. If the signals are equal the detector output will fall to zero when the phase shifter is appropriately adjusted. In the actual apparatus the signals were very nearly equal and the phase shifter was adjusted for minimum signal.

As the horn spacing was decreased, the phase shifter was adjusted for the best minimum at each increment of distance and recorded. In addition, the signal level between the two arms was balanced by changing the level with the calibrated attenuator in the water arm. A variable phase shift which was associated with this attenuation variation was corrected for by methods described later.

The equations for n and k were based on the assumption that a TEM wave was incident on the receiving horn. The accuracy of this assumption was checked by measuring the change of intensity as the horn separation was decreased. Since the amplitude must vary linearly in db with distance the horns were closed until this was no longer true, indicating that a TEM wave was no longer incident on the receiving horn. This occurred at a horn separation of 0.4 mm. All measurements were taken between 0.4 and 3.4 mm separation. A sample calculation is given later for both n and k.

THEORY OF HOMOGENEOUS DIELECTRICS

In the general theory of homogeneous dielectrics it is found that the structure and dielectric properties of the atoms and molecules lead to a system of classification.

If the molecules are non-polar it is only necessary to consider the fields which cause a distortion of the atoms. Thus, if an atom is subjected to an external field E, an electric dipole moment m_o is induced. The electrical properties may therefore be described by a constant polarizability p_o, so that

$$m_o = p_o E.$$

This gives rise to the so called optical or electronic polarization since it is caused by a displacement of the charges in the electron orbits at optical frequencies. This has been substantiated both theoretically and experimentally by Lorenz, Clausius, Mosotti, and recently by Van Vleck who has derived the electrical properties from the quantum mechanical viewpoint.

When the medium contains polar molecules it is necessary to consider components in addition to the one indicated above. Three effects exist: (1) the elastic displacement of the charges produces an appreciable field at frequencies in the infra-red region and gives rise to the atomic polarization; (2) the change in the average orientation of the molecule produces a component of polarization called the molecular polarization; and (3) there may be non-electrostatic forces which reduce the contribution to the polarization caused by the change in dipolar orientation.

On the basis of those effects, homogeneous dielectric materials are divided into three main groups:

1. Substances which show only electronic polarization,
2. Polar substances which have both electronic and atomic polarization, and
3. Polar substances which also exhibit polarization due to the effects of dipolar orientation.

Both Debye and Onsager have treated a polar liquid theoretically. Each has introduced the concept of relaxation time of the molecule which describes as an exponential decay function the properties of a dielectric substance in a time varying field after being rotated by the field. Regardless of the theory employed, an accepted expression for the complex dielectric constant in the region of loss or anamolous dispersion is

$$K = K' - jK'' = K_o + \frac{K_s - K_o}{1 - j\omega\tau} \qquad (15)$$

where K_o is the dielectric constant due to the electronic and atomic polarization, K_s is the static dielectric constant, $\omega = 2\pi f$ where f is the frequency in cycles per second, and τ is the relaxation time of the molecule in seconds.

If the real and imaginary quantities of equation (14) are separately equated it is found that

$$K' = K_o + \frac{K_s - K_o}{1 + \omega^2 \tau^2} \qquad (16)$$

and

$$K'' = -\frac{\omega\tau(K_s - K_o)}{1 + \omega^2\tau^2} . \qquad (17)$$

The variation of the static dielectric constant K_s with temperature[6] is known and K_o can be considered as relatively constant over the temperature range 0° - 50°C. Table I presents values of K_s, K_o, and τ due to Saxton and Lane[7]. In a private communication Dr. J. A. Saxton has reported that recent measurements give an average value of 4.9 for K_o.

TABLE I

DIELECTRIC PROPERTIES OF WATER

Temperature ($^\circ$C)	K_s	K_o	τ (Sec.)
0	88.0	4.5	21.0×10^{-12}
5	86.0	5.0	15.1
10	84.0	5.5	11.6
15	82.0	5.5	8.9
20	80.0	5.4	7.7
30	76.4	5.3	5.8
40	73.0	5.2	4.7

It has been previously shown that the complex dielectric constant may be written in terms of the complex index of refraction:

$$K' = n^2 - k^2 \text{ and } K'' = 2nk. \qquad (18)$$

If equations (16) and (17) are substituted into (18) and the

result solved for n and k there results

$$2n^2 = \sqrt{\frac{K_s^2 + K_o^2\omega^2\tau^2}{1+\omega^2\tau^2}} + \frac{K_s + K_o\omega^2\tau^2}{1+\omega^2\tau^2} \qquad (19)$$

and

$$2k^2 = \sqrt{\frac{K_s^2 + K_o^2\omega^2\tau^2}{1+\omega^2\tau^2}} - \frac{K_s + K_o\omega^2\tau^2}{1+\omega^2\tau^2} \cdot \qquad (20)$$

These two expressions are derived in the appendix; together with the values in Table I they lead to the theoretical curves used in the following section.

It should be pointed out that the curves indicated as theoretical are determined by using experimental values of K_s, K_o, and τ. Saxton and Lane made experimental measurements at 19,000 Mc. and 24,000 Mc. to obtain the values of K_o and τ in Table I. It was the purpose of this investigation to show that these values are valid at higher frequencies and in particular at 35,000 Mc. The experimental results in the next section indicate that this is true. In fact one should be able to calculate with reasonable accuracy the index of refraction and the absorption coefficient of water at even higher frequencies than those reached in this investigation.

DISCUSSION OF THE EXPERIMENTAL RESULTS

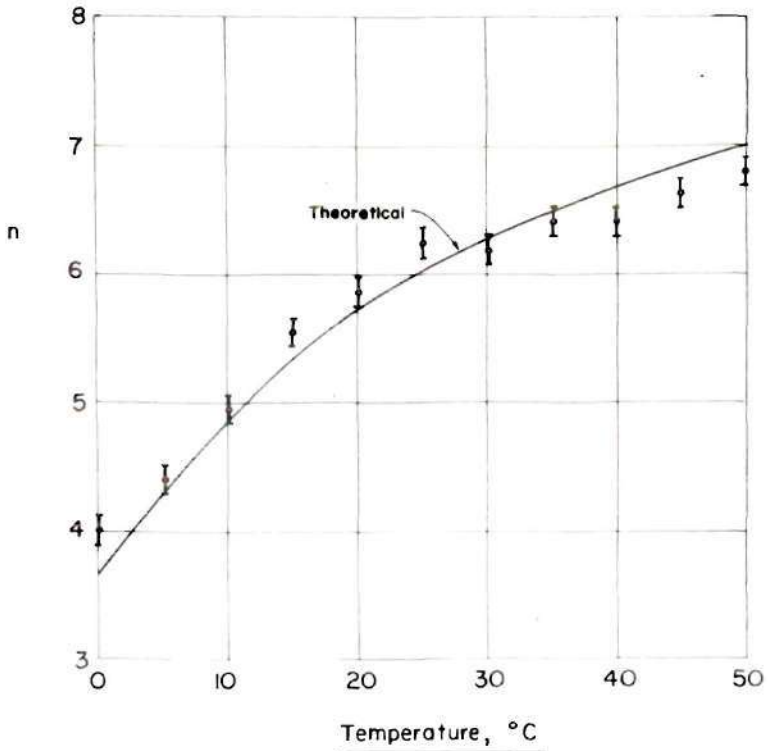
The experimental measurements were made over a temperature range of 0°-50°C. in an effort to obtain direct experimental data in the 35,000 Mc. region of the spectrum. The values of n and k were calculated using equations (9a) and (10a) with the measured values given in Table II. The tabulated values are the average of a minimum of five readings at each temperature. The theoretical curves are those obtained from equations (19) and (20). The range of temperatures used was considered to be the most useful for engineering applications.

TABLE II

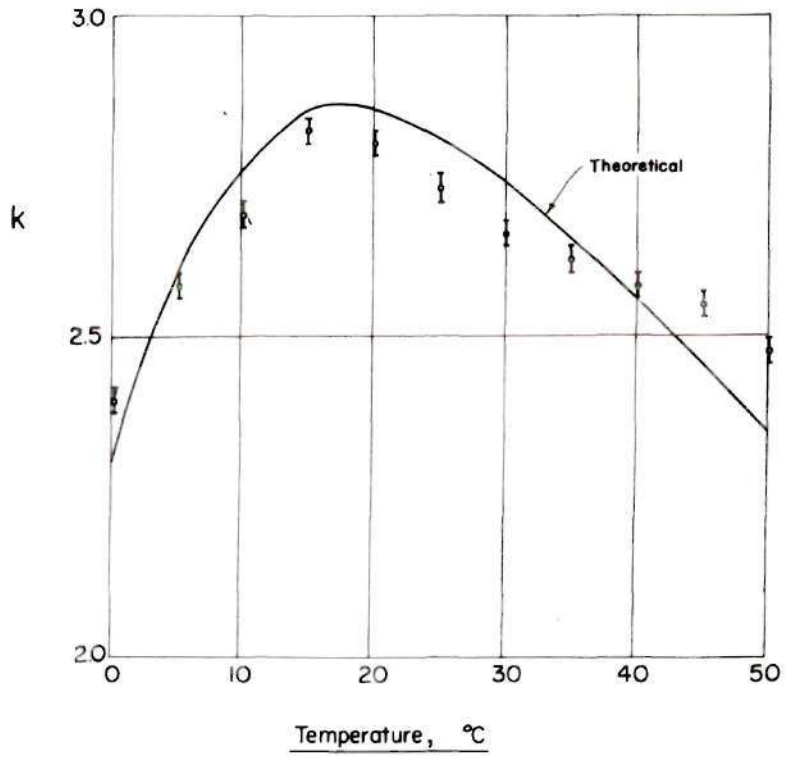
ATTENUATION AND PHASE SHIFT OF WATER

Temperature ($^{\circ}$C)	α (db/mm)	β (radians/mm)
0	15.3	2.93
5	16.4	3.22
10	17.1	3.63
15	17.9	4.07
20	17.8	4.30
25	17.2	4.58
30	16.9	4.53
35	16.65	4.70
40	16.45	4.69
45	16.25	4.86
50	15.8	4.98

The agreement between the theoretical curves derived by the Onsager expression and the experimental results is very close as an examination of Figures 5 and 6 will show. Figure 5 represents the variation of n and k with temperature. In both instances the



Refractive Index of Water, 35,000 Mc.



Absorption Coefficient of Water, 35,000 Mc.

Figure 5

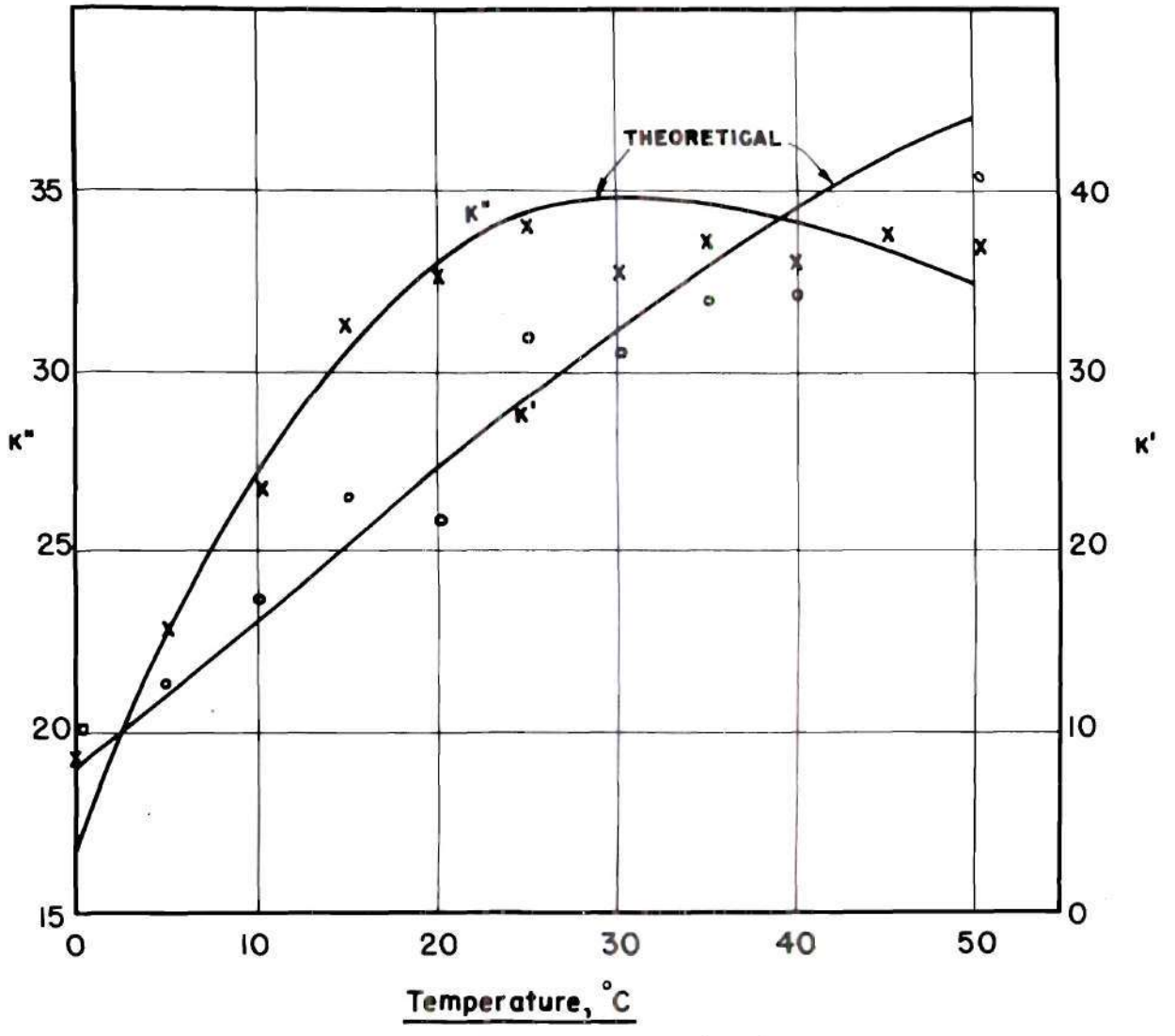
experimental points lie along the theoretical curve and in many cases agree exactly. The experimental points indicate all the known errors in the system. However, errors such as temperature gradients across the water path between the horns, errors in reading, backlash in the horn assembly, and a multiplicity of small cumulative errors may well explain what deviation there is between the theoretical and experimental curves.

Figure 6 shows the real and imaginary components of the complex dielectric constant versus temperature. Here the deviation is more pronounced. It should be remembered that K' is proportional to the difference of n^2 and k^2 while K'' is proportional to the product of n and k; thus small experimental errors are likely to appear magnified when the complex dielectric constant is calculated. This is due to the fact that n and k are the directly measured quantities from which the complex dielectric constant must be calculated.

Figure 7 shows the calculated index of refraction and the absorption coefficient of water at $20^{\circ}C$ over the wavelength region from 2 mm to 10 cm. It is seen from the shape of the k curve that this wavelength spread covers practically the entire region where the anamolous dispersion of water occurs. The experimental values obtained in this research are shown in relation to those obtained by Saxton and Lane at longer wavelengths. Here again the results are in substantial agreement with those theoretically obtained.

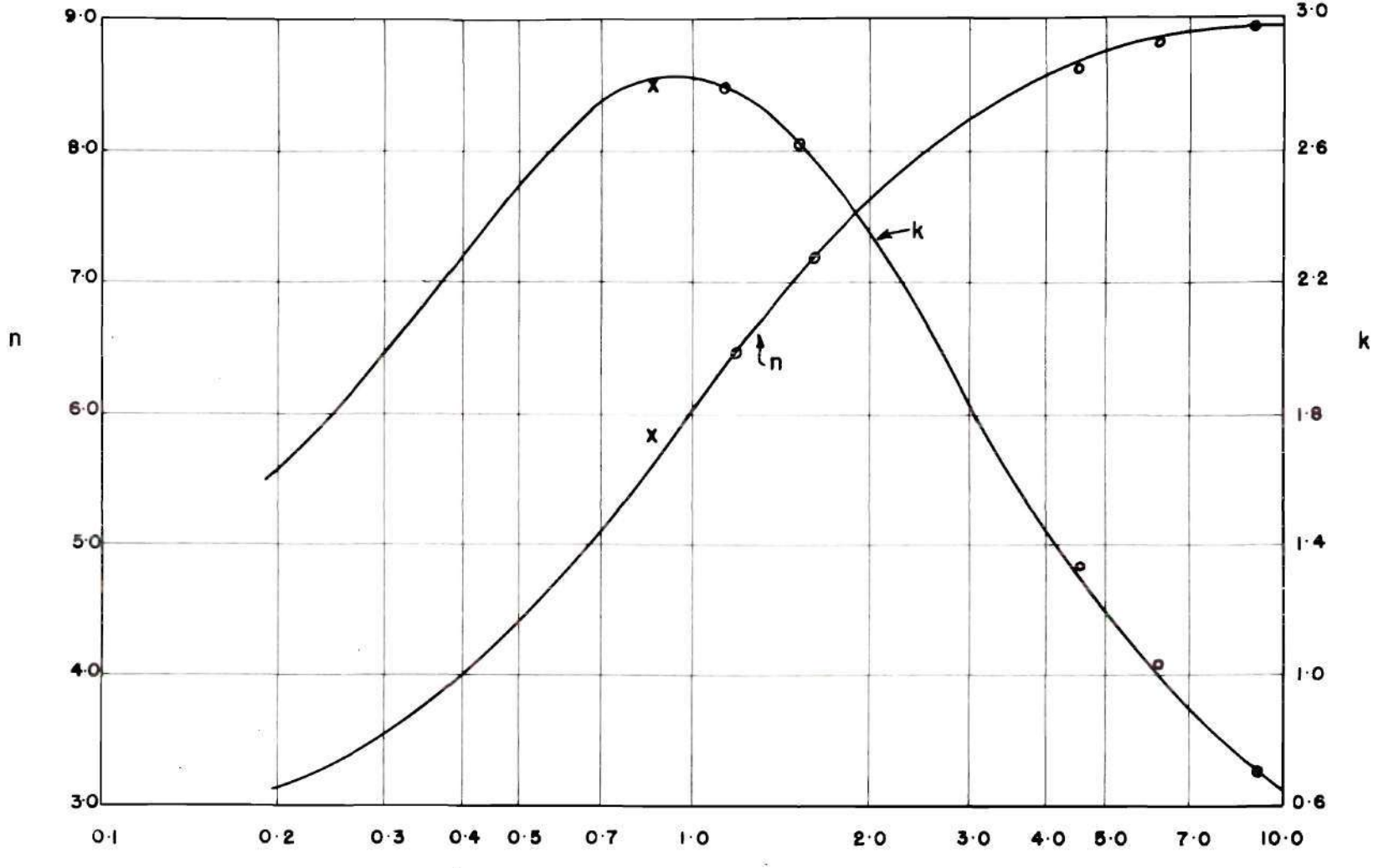
Accuracy

An experimental system of the type used has many pitfalls. Some of these may be avoided by proper design of the system; however, many



Complex Dielectric Constant of Water, $\kappa = \kappa' - j\kappa''$, 35,000 Mc.

Figure 6



Variation of k and n of Water with Wave-Length. Temperature 20°C.

o – Saxton and Lane.

x – Honer

Figure 7

result from the use of extreme short wavelength of the radiation and the close mechanical tolerances this imposes for accurate quantitative measurements. The attenuator must be calibrated for phase shift as well as attenuation because the attenuator card produces a phase shift as it is inserted into the wave guide. For high experimental accuracy the phase shift must be known to $\pm 4^{\circ}$ and the attenuation to $\pm$ 0.1 decibel. The dielectric phase shifter must also be calibrated to the same tolerances. In general, the attenuator calibration was determined by use of a bolometer whose characteristics were assumed to be square law. This relationship exists when the bolometer bias current is high compared to the current induced by the electromagnetic radiation. The phase shift was measured with the aid of a slotted section and an adjustable shorting plunger. Since the attenuator is calibrated for a matched line, an E-H matching section was placed in the system so that the mismatch between the transmitting horn and the water cell produced no appreciable standing waves in the wave guide, as required for accurate attenuation measurements. This may be seen in Figure 3 just after the slotted section.

A major mechanical problem is encountered when the horns are moved, since variations from parallelism of 0.001 inches will result in large and unpredictable experimental errors. The elaborate harness required for this purpose can be seen in detail in Figure 4. In general, the better the mechanical workmanship, the better will be the experimental results.

Sample Calculation at 20°C

The measurement frequency of 35,000 Mc. corresponds to a free-space

wavelength, λ_o, of 8.57 mm. From Table II the attenuation, α, was measured as 17.8 db/mm. Using equation (9a) one may calculate the absorption coefficient as follows:

$$k = 0.01835\ \lambda_o \alpha$$
$$= 0.01835 \times 8.57 \times 17.8$$
$$= 2.80 .$$

Similarly, the index of refraction is calculated from equation (10a) where the phase shift, β, is measured in radians per millimeter. The value tabulated is that after the correction for the phase shift of the calibrated attenuator was subtracted. Therefore,

$$n = \lambda_o \beta / 2\pi$$
$$= 8.57 \times 4.30/2$$
$$= 5.87$$

CONCLUSIONS

The experimental method described provides a means for the measurement of the dielectric properties of water as well as other liquids in the 35,000 Mc. region. Accuracy of the results is dependent upon the mechanical tolerances that are maintained within the waveguides and the water cell. A system of this type should be applicable to frequencies as high as 60,000 Mc.

The experimental results satisfactorily substantiate the values of relaxation time and the optical-frequency dielectric constant of the water molecule as determined by Saxton and Lane. Therefore, one should be able to calculate the dielectric properties of water at temperatures between 0°-50°C over the region of 3,000 - 35,000 Mc. with great accuracy. In addition, there is reason to believe that the equations are valid to frequencies as high as 100,000 Mc.

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APPENDIX

APPENDIX

DERIVATION OF THE COMPLEX INDEX OF REFRACTION

Both Debye[2] and Onsager[4] have developed expressions for the behavior of a polar molecule in a periodic field. The final expressions are identical from a mathematical viewpoint. Their basic difference lies in the value of τ the relaxation time of the molecule, which must be determined from experimental measurements. Therefore, an accepted expression for the complex dielectric constant in the region of anamolous dispersion is

$$K' - jK'' = K_o + \frac{K_s - K_o}{1 - j\omega\tau} \tag{A1}$$

Transposing K_o to the left and rationalizing the expression one obtains

$$K' - K_o - jK'' = \frac{K_s - K_o + j\,\omega\tau(K_s - K_o)}{1 + \omega^2\tau^2} . \tag{A2}$$

By separately equating the real and imaginary components one may obtain

$$K' = K_o + \frac{K_s - K_o}{1 + \omega^2\tau^2} \tag{A3}$$

and

$$K'' = - \frac{\omega\tau(K_s - K_o)}{1 + \omega^2\tau^2} \tag{A4}$$

It has already been shown that $K' = n^2 - k^2$ and $K'' = 2nk$; therefore

$$n^2 - k^2 = K_o + \frac{K_s - K_o}{1 + \omega^2 \tau^2} \tag{A5}$$

and

$$2nk = - \frac{\omega \tau (K_s - K_o)}{1 + \omega^2 \tau^2} \tag{A6}$$

In order to simplify expressions (A5) and (A6) let

$$A = \frac{K_s - K_o}{1 + \omega^2 \tau^2} \tag{A7}$$

therefore

$$n^2 - k^2 = K_o + A \tag{A8}$$

and

$$2nk = - \omega \tau A. \tag{A9}$$

Solving the latter for k and substituting in equation (A8) one obtains

$$n^2 - \frac{\omega^2 \tau^2 A^2}{4n^2} = K_o + A. \tag{A10}$$

Now multiply by n^2 and transpose and collect all terms of a like power so that

$$n^4 - (K_o + A)n^2 - \frac{\omega^2 \tau^2 A^2}{4} = 0 . \tag{A11}$$